Airborne measurements of CO, O$_3$, NMHCs and aerosol scattering in the Northeast Pacific during PHOBEA-II

Heather Umbehocker Price, Paul V. Doskey and Daniel A. Jaffe

At Paine field in Everett, WA before a PHOBEA II flight. From left: Heather Price, Dan Jaffe and the pilot Richard

The PHOBEA II ground observations took place at Cheeka Peak Observatory (CPO), located in the northwest corner of Washington State. Aircraft observations were conducted in the vicinity of CPO.

PHOBEA II

During the spring of 2001 we measured a wide array of gaseous and aerosol species as part of the PHOBEA-2 experiment. Measurements were made both on the ground and using the twin engine Beechcraft Duchess aircraft shown above. Species measured include CO, O3, NMHCs, Hg, aerosol scattering and aerosol chemistry.

The primary objectives for PHOBEA II are:

1. to improve our understanding of the sources, sinks and other factors controlling the distributions of these compounds in the northeastern Pacific

2. to investigate the combined effects of chemistry and transport on the concentrations we observe

3. to help validate a variety of global chemical transport models (CTMs) which are being applied to atmospheric chemistry in the Pacific.

This poster presents an overview of the PHOBEA II spring 2001 campaign with an emphasis on how non-methane hydrocarbon (NMHC) will be analyzed and used.

Differences between PHOBEA I and II:

PHOBEA 2 has a wider suite of studies to compare with than PHOBEA 1. These include PEM-West B, ACE-ASIA and TRACE-P. Since ACE-ASIA and TRACE-P were concurrent with PHOBEA 2 there is an opportunity to study the same or at least similar air masses thus giving more accurate comparisons, hydrocarbon ratio analysis of transit times, correlations, trajectory analysis and global chemical transit model validation.

During PHOBEA 1 a limited number of VOC and CO measurements were taken (about 4 canisters per flight ranging over 8 km altitude). Most of the canisters (30) were used to sample 0-4km while only 14 canisters sampled the upper region between 4-8 km. In subsequent modeling studies and analysis it is suggested that most pollution is transported above 4km. For PHOBEA 2 we collected a total of 75 canister samples for CO and VOCs. 36 samples were collected above 4km and 34 below 4 km.

Future Studies

Fall 2001
- Aircraft and ground study similar to PHOBEA 2
- First time for fall study

Spring 2002
- aircraft and ground study
- Co-PI at University of Wasington Lyatt Jeagle, GEOS-Chem model
- New Fast-CO instrument
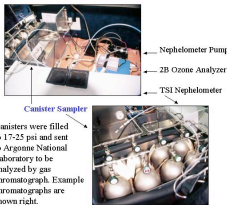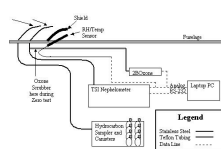- Concurrent NOAA experiment including 2 aircraft, 1 ship

Aircraft Interior Layout

For aircraft observations we used a Duchess Beechcraft twin engine aircraft (pictured above).

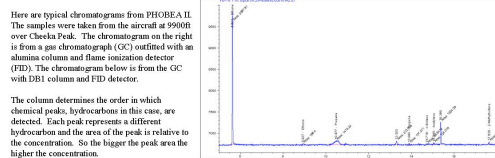Below is a photo of the interior of the aircraft. The canister sampler was used to collect NMHC and carbon monoxide samples.

- Nephelometer Pump
- 2B Ozone Analyzer
- TSI Nephelometer

Canister Sampler

Canisters were filled to 17-25 psi and sent to Argonne National Laboratory to be analyzed by gas chromatograph. Example chromatographs are shown right.

Beachcraft Duchess Flow & Wiring Diagram

Chromatograms from PHOBEA II

Here are typical chromatograms from PHOBEA II. The samples were taken from the aircraft at 9900ft over Cheeka Peak. The chromatogram on the right is from a gas chromatograph (GC) outfitted with an alumina column and flame ionization detector (FID). The chromatogram below is from the GC with DB1 column and FID detector.
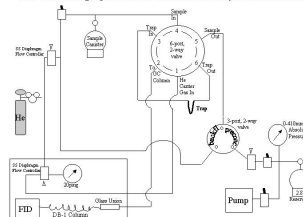
The column determines the order in which chemical peaks, hydrocarbons in this case, are detected. Each peak represents a different hydrocarbon and the area of the peak is relative to the concentration. So the bigger the peak area the higher the concentration.

Gas Chromatograph with Pre-concentration System Schematic

Because the concentrations of NMHC in the in ambient air is low, in the parts per billions range, a preconcentration system is necessary to cryofocus the sample before introduction onto the gas chromatograph column. Each GC has its own preconcentration system.

Why measure Non-methane hydrocarbons, (NMHC)?

NMHC can be used to determine:
- transit times/photochemical age
- source regions
- air mass history and removal processes
- validate chemical transport models

Seasonality of transit time
- Meteorology and models suggest slow summer/fall and fast winter/spring
- Will hydrocarbon ratios tell the same story?

NMHC lifetimes vary allowing photochemical aging of air masses
- Butane lifetime ~ 5 days
- Propane lifetime ~ 10 days
- Ethane lifetime ~ 50 days

NMHC Photochemical Reactions

Hydroxyl formation:
$$O_3 + h\nu \ (\lambda \leq 420nm) \rightarrow O(^1D) + O_2$$
$$O(^1D) + H_2O \rightarrow 2OH\bullet$$

NMHC oxidation to peroxyalkyl radical:
$$RH + OH\bullet \rightarrow R\bullet + H_2O$$
$$R\bullet + O_2 + M \xrightarrow{\text{fast}} RO_2\bullet + M$$

Peroxyalkyl radical lead to hydroperoxy radical:
$$RO_2\bullet + NO \rightarrow NO_2 + RO\bullet$$
$$RO\bullet + O_2 \rightarrow RO + HO_2\bullet$$
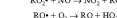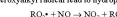
Hydroperoxy radical reaction with NO creates O$_3$:
$$HO_2 + NO \rightarrow NO_2 + OH\bullet$$
$$NO_2 + h\nu \ (\lambda \leq 420nm) \rightarrow NO + O(^3P)$$
$$O(^3P) + O_2 + M \rightarrow O_3 + M$$

Photochemical Age from Hydrocarbon Ratios

Using two NMHCs with varying lifetimes, like propane and ethane, allow determination of the photochemical age of an air masses.

Propane has a lifetime around 10 days which is on par with the transit time from the Asian continent to the North Pacific. Meanwhile the ethane lifetime is much longer, close to two months.

The difference in lifetimes, neglecting dilution, creates a photochemical clock as propane concentrations decrease sharply during transit compared with ethane concentrations.
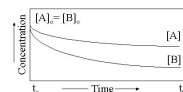
Calculating Hydrocarbon Ratios

Neglecting dilution, light alkanes follow pseudo first order reaction with OH:

$$[A] = [A]_0 \exp{-k_A[OH]t}$$

Two NMHCs with varying lifetimes and known initial concentrations allow determination of photochemical age:

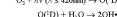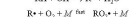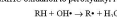$$\ln\frac{[A]}{[B]} = \ln\frac{[A]_0}{[B]_0} - (k_A - k_B)[OH]t$$

k = rate constant
t = photochemical age
[OH]≅1x106 molecules cm-3

$[A]_0 = [B]_0$

NO-rich environments [NOx]>1ppb:
- production of ozone
- production of hydroxyl radicals
- production of CO2

$$CO + OH\bullet \rightarrow H\bullet + CO_2$$
$$H\bullet + O_2 + M \rightarrow HO_2\bullet + M$$
$$HO_2\bullet + NO \rightarrow HO\bullet + NO_2$$
$$NO_2 + h\nu \ (\lambda \leq 410nm) \rightarrow NO + O$$
$$O + O_2 + M \rightarrow O_3 + M$$
Net: $CO + 2O_2 + h\nu \rightarrow CO_2 + O_3$
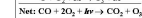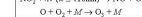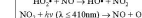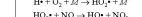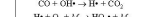
NO-poor environments [NOx]< 30ppt:
- destruction of ozone
- production of CO2

$$CO + OH\bullet \rightarrow H\bullet + CO_2$$
$$H\bullet + O_2 + M \rightarrow HO_2\bullet + M$$
$$HO_2\bullet + O_3 \rightarrow HO\bullet + 2O_2$$
Net: $CO + O_3 \rightarrow CO_2 + O_2$